Indian J. Phys. **71A** (5), 545–554 (1997)

IJP A
— an international journal

X-ray, thermal and dielectric properties of $A_{15}La_{38}Ti_{72}O_{216}$ (A = Ca, Sr, Ba) ceramics

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Received 11 October 1996 accepted 6 May 1997

Abstract : The polycrystalline samples of $A_{15}La_{38}Ti_{72}O_{216}$ (A = Ca, Sr, Ba) were prepared by high temperature solid-state reaction technique. Preliminary structural analysis of the compounds from the X-ray powder data show that these compounds are orthorhombic at room temperature. Detailed dielectric and thermal studies in a wide temperature range did not show any anomaly which could support the predicted ferroelectricity in the above compounds

Keywords : Polycrystalline ceramics, structural analysis, dielectric and thermal studies

PACS Nos. : 77 22.Gm, 61.10.Nz, 77 80.Bh

1. Introduction

Since the discovery of an interesting ferroelectric properties in perovskite $BaTiO_3$ [1], the crystal structure and physical properties of a large number of pure and complex oxides of different structures and chemical compositions have been examined [2–8], in search of new ferroelectric for device applications. Some compounds (*i.e.* $BaTiO_3$, $LiNbO_3$, $KTaO_3$, $Pb(ZrTi)O_3$, $LaTiO_3$, $PbNbO_3$ *etc.*) of perovskite and tungsten bronze families [9–13] have been found very useful for many devices such as computer memory, display, electro-optic modulator, transducer, pyroelectric detector, IR sensor *etc.* Though the crystal structure of the tungsten bronze (TB) is much more complicated [14] compared to the perovskite structure [15], a large number and variety of compounds of TB family with large variation of physical properties can be prepared which can be useful for devices. In search of new materials of the TB family, ferroelectricity in one of its large molecule numbers $Ba_{15}Pr_{38}Ti_{72}O_{216}$ has been predicted recently [16], on the basis of its crystal structure. As a part of the systematic and extensive studies of ferroelectric properties of TB family, we have carried out structural, thermal and dielectric properties of the titled compounds to find out the existence of predicted ferroelectric properties in them.

2. Experimental

The polycrystalline samples of $A_{15}La_{38}Ti_{73}O_{316}$ (A = Ca, Sr, Ba) were prepared by high temperature solid-state reaction technique using high purity $CaCO_3$ (M/S Glaxo Laboratories (I) Ltd.), $SrCO_3$ (M/S Burgoyne Urbiages & Co.), $BaCO_3$ (AR Grade BDH), La_2O_3 (M/S Indian Rare Earth Ltd.) and TiO_3 (M/S s.d.fine-chem. Pvt. Ltd.) in a stoichiometry. The weighted ingredients were thoroughly mixed in an agate mortar for two hours. The powders of these compounds were calcined at 1000°C in pure alumina crucibles for 24 hours in an air atmosphere. The calcined powders were again ground and calcined at the same temperature in order to complete the reaction and formation of the desired compounds. Finally, the fine homogeneous powders of all the three compounds were used to make cylinderical pellets of 10 mm diameter and 1–2 mm thickness at a pressure of 6×10^7 kg/m^2 using hydraulic press. As it was difficult to make pellets with very fine powders, polyvinyl alcohol (PVA) was used as binder. The pellets were then sintered at 1200°C for 24 hours in silicon carbide high temperature furnace and in alumina crucible. The formation of the single phase compound were checked by X-ray diffraction profile.

For preliminary structural analysis of all the compounds at room temperature, X-ray powder diffraction profiles were recorded using X-ray powder diffractometer (Miniflex JXR, Japan) with CuKα radiation (λ = 0.15418 nm) in an wide range of Bragg angle 2θ ($10° \leq 2\theta \leq 90°$) at a scanning rate of 2°/minute. To examine the grain/particle size and their distribution on the surfaces of the compounds, the scanning electron micrographs (SEM) at a particular magnification were taken using a computer controlled Stereoscan/CAMSCAN S-180 scanning electron microscope. To study the electrical/dielectric properties of the compounds, both the flat surfaces of the pellets were polished and electroded with high purity fine particle silver paste. The capacitance and the dissipation factor of all the samples were measured using GR 1620 AP capacitance measuring assembly as a function of frequency (10^3 Hz to 10^4 Hz) and as a function of temperature (−160°C to 250°C). In order to check the thermal stability of the title compounds, thermal curves (TG, DTA) were recorded from room temperature to 600°C.

3. Results and discussion

In Figure 1, room temperature X-ray diffraction patterns of all the three compounds have been compared of which sharp single peaks suggest the formation of single phase compound. All the observed peaks are different in position and intensity from their starting materials. With the observed *d*-values obtained from diffraction patterns, reflection peaks of the compounds were indexed and their unit cell parameters were determined in different cell configuration/crystal systems. A suitable unit cell of the compounds were selected on the basis of the best agreement in the observed and calculated *d*-values. Finally, the selected cell dimensions of the compounds were refined using different options of the standard computer programme, "POWDER PACKAGE". With the refined cell parameters. The *d*-

values of all the reflections were again calculated and compared with their observed values. The orthorhombic cell parameters of all the compounds have been tabulated and compared

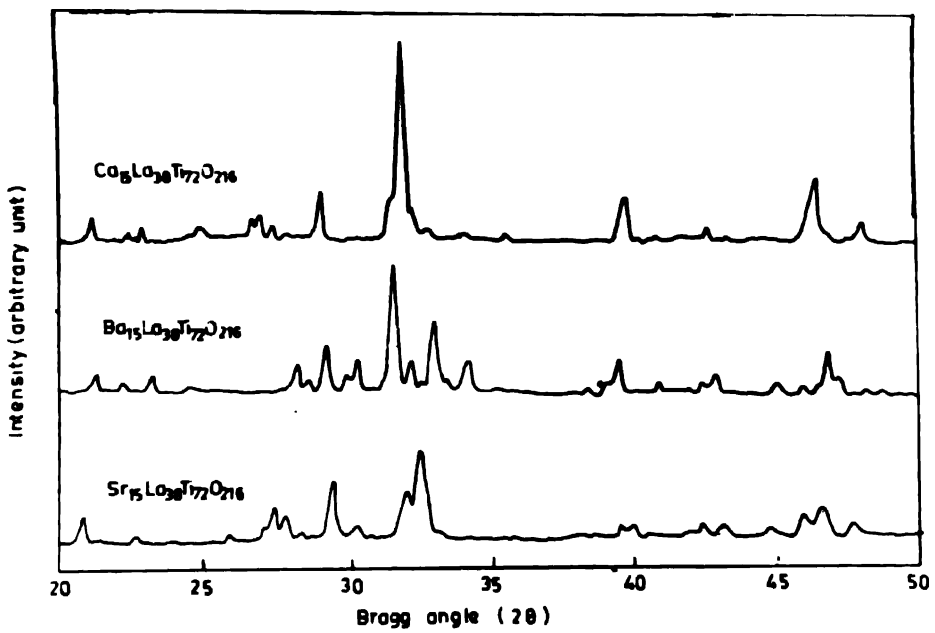

Figure 1. Comparison of room temperature X-ray diffraction patterns of $A_{15}La_{38}Ti_{72}O_{216}$ (A = Sr, Ba, Ca) compounds.

in Table 1. The observed and calculated *d*-values of all the compounds were found in very good agreement (Tables 2–4) which suggest the correctness of the selected unit cell and

Table 1. Comparison of lattice parameters, particle size from X-ray patterns and SEM in parenthesis, density and activation energy of $A_{15}La_{38}Ti_{72}O_{216}$ (A = Ca, Sr and Ba).

Compound	Lattice parameters (Å)	Particle size (Å)	Density (gm/cc)	Activation energy (ev)
$Ca_{15}La_{38}Ti_{72}O_{216}$	a 08.3814 b 12.2075 c 12.9230	424 (540)	6.41	0.164
$Sr_{15}La_{38}Ti_{72}O_{216}$	a 09.6243 b 12.1120 c 13.0380	383 (490)	6.59	0 239
$Ba_{15}La_{38}Ti_{72}O_{216}$	a 10.0238 b 12.9268 c 09.7061	256 (337)	6.77	0 095

structure. From the preliminary structural analysis, it has been found that the crystal structures of all the compounds are orthorhombic at room temperature.

Table 2. Comparison of observed and calculated d-values (Å) and intensity ratio of some reflections of $Sr_{15}La_{38}Ti_{72}O_{216}$.

Sl No	h k l	d_{obs} in (Å)	d_{cal} in (Å)	I/I_0
1.	0 2 0	7.7618	7.7618	10
2.	2 0 0	6.4634	6.4634	3
3.	2 1 1	4 2104	4.2104	11
4.	0 3 1	3.9001	3 9022	7
5.	3 0 1	3 4795	3.4795	8
6	0 4 1	3 2549	3.2492	11
7.	4 0 0	3 2090	3.2317	12
8	4 1 0	3 1644	3.1639	8
9.	4 2 0	2 9980	2 9834	24
10	0 5 1	2 7466	2 7517	100
11	1 2 2	2.7142	2 7129	16
12	4 2 1	2 6671	2 6662	7
13	3 4 1	2.5996	2.5943	3
14	4 3 1	2 4946	2 4890	2
15	4 5 0	2 2432	2 2389	22
16	1 7 0	2 1859	2.1857	2
17.	4 2 2	2 1034	2 1052	6
18	6 2 0	2.0758	2 0760	3
19.	5 0 2	1.9489	1 9503	33
20	5 5 1	1 8842	1 8842	8
21.	6 5 0	1 7712	1.7700	2
22	4 0 3	1 6894	1 6687	6
23	7 3 1	1.6695	1.6692	3
24.	7 5 0	1.5851	1 5871	30

Table 3. Comparison of observed and calculated d-values (Å) and relative observed intensity of some reflections of $Ba_{15}La_{38}Ti_{72}O_{216}$.

Sl No.	h k l	d_{obs} in (Å)	d_{cal} in (Å)	I/I_0
1	1 2 0	5 1257	5.1257	18
2	1 2 1	4 7703	4 7703	9
3	2 1 1	4 2302	4.2302	16
4.	0 3 0	4 0401	4 0373	10
5.	2 0 2	3.8667	3.8716	11
6	0 2 3	3.4950	3 5309	4
7	3 0 0	3.1977	3.2081	20
8.	1 0 4	3.0789	3.0872	36
9	1 1 4	2 9980	2.9916	9
10	0 3 3	2.9592	2.9579	21
11	2 2 3	2 8488	2.8468	100

Plate I

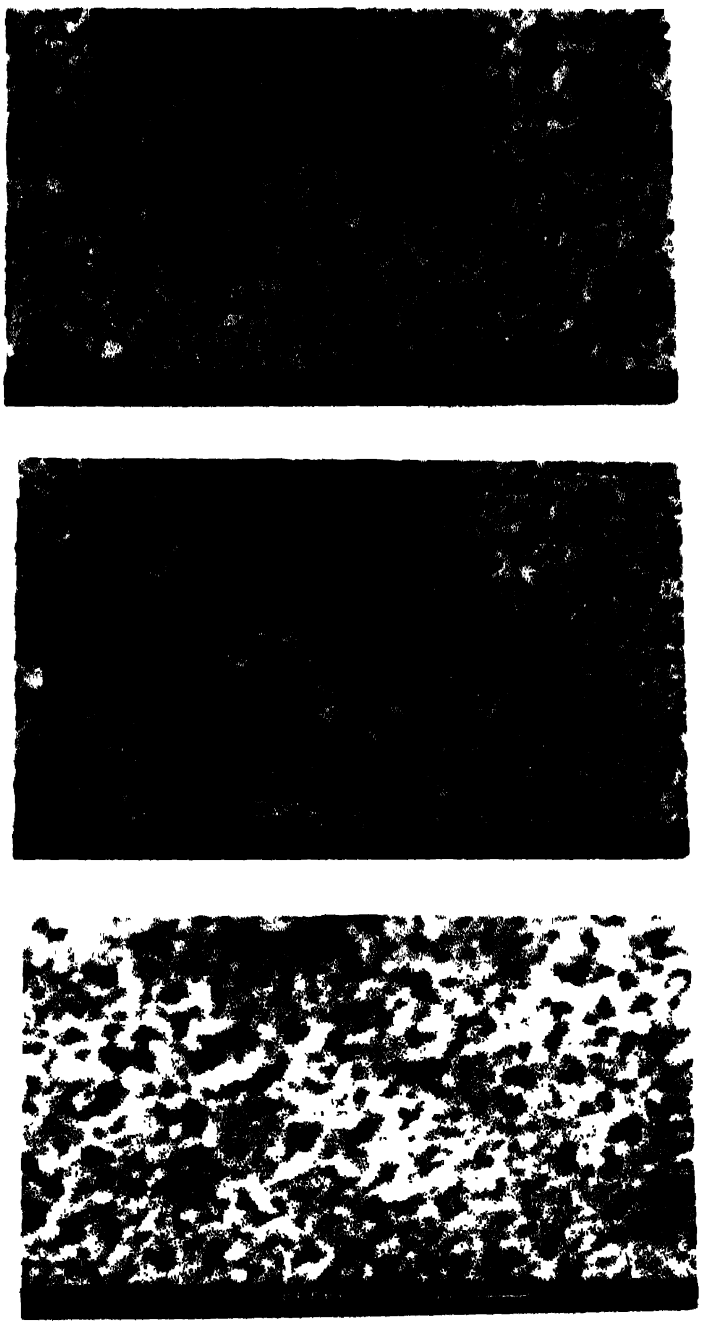

Figure 2. Comparison of SEM micrographs of the $A_{15}La_{38}Ti_{72}O_{216}$ (A = Sr, Ba, Ca) ceramic compounds.

Table 3. *(Cont'd.).*

Sl No.	h k l	d_{obs} in (Å)	d_{cal} in (Å)	I/I_0
12.	2 3 2	2 7967	2 7944	18
13	0 4 2	2 7303	2.7462	45
14.	2 0 4	2 6983	2 6987	4
15	2 1 4	2 6367	2 6367	18
16	0 1 5	2.5495	2.5492	4
17	4 1 0	2.3559	2.3600	4
18	2 0 5	2.2924	2 2926	27
19	1 5 2	2.2115	2.2100	9
20	2 5 1	2 1317	2 1345	11
21	4 2 2	2.1127	2 1151	14
22	2 4 4	2.0144	2 0147	9
23	0 4 5	1 9770	1.9759	7
24	4 4 0	1 9371	1.8838	34
25	0 2 7	1 8842	1 7803	4
26.	5 1 3	1 7814	1 7417	9
27.	0 7 0	1 7429	1 7303	11
28.	2 2 7	1.7303	1 6697	7
29	1 5 6	1 6695	1.5952	4
30	2 7 2	1 5951	1 5797	27

Table 4. Comparison of observed and calculated d-values (Å) and intensity ratio of some reflections of $Ca_{15}La_{38}Ti_{72}O_{216}$.

Sl. No	h k l	d_{obs} in (Å)	d_{cal} in (Å)	I/I_0
1.	0 0 1	4 1907	4 1907	27
2	1 1 1	3.8833	3 8833	13
3	1 2 1	3.4012	3 4012	10
4.	6 0 0	3.2203	3 2308	33
5	4 0 1	3.1754	3.1699	27
6.	6 1 0	3.1210	3.1232	10
7.	1 4 0	2.9980	3 0147	67
8.	0 3 1	2.9214	2 9194	17
9.	5 1 1	2.7714	2.7716	53
10.	3 4 0	2.7385	2.7596	100
11.	4 3 1	2.4946	2.5007	3
12.	8 2 0	2.2539	2 2521	17
13.	6 4 0	2.2325	2.2185	13

Table 4. *(Cont'd.)*

Sl No	h k l	d_{obs} in (Å)	d_{cal} in (Å)	I/I_0
14	9 1 0	2.1317	2.1211	7
15	0 5 1	2.1034	2.1096	17
16.	5 4 1	2.0758	2.0814	13
17	3 5 1	2.0060	2.0054	10
18	6 4 1	1 9529	1.9607	24
19	4 5 1	1.9332	1 9343	33
20	9 1 1	1 8879	1 8925	13
21	6 5 1	1.7744	1.7664	10
22	6 2 2	1 6893	1.6893	10
23	3 4 2	1 6695	1.6688	10
24	4 4 2	1 6260	1 6271	7
25	5 4 2	1 5801	1 5779	20

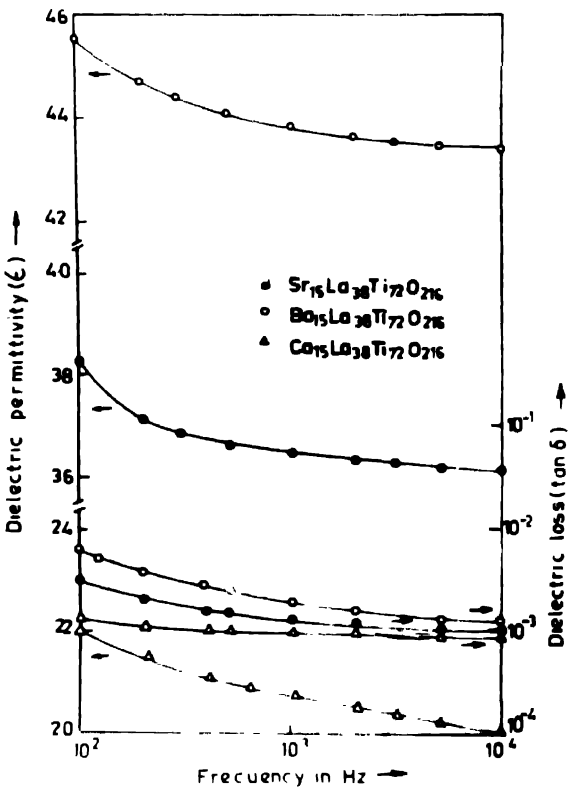

Figure 3. Variation of ε' and tan δ of $A_{15}La_{38}Ti_{72}O_{216}$ (A = Sr, Ba, Ca) compound as a function of frequency

The linear particle size of the samples were calculated from some strong reflections of different 2θ angle using Scherrer's equation, the average value of those are given in Table 1, which are consistent with the particle size obtained from SEM. The SEM

micrographs obtained from gold coated pellets at 3 μm magnification for different compounds have been compared in Figure 2 which show uniform distribution of spherical particles. However, some holes/voids have been found which confirm low density of the pellets. Measured densities of the pellet samples for different compounds are given in Table 1.

In Figure 3, the variation of dielectric constant (ε) and dielectric loss (tan δ) of the compounds with frequency have been compared. The normal trend and behaviour of a dielectric are found in studied compounds. At 10 KHz, the variation of ε and tan δ from −160°C to 250°C of all the compounds have been compared in Figure 4. It is observed that

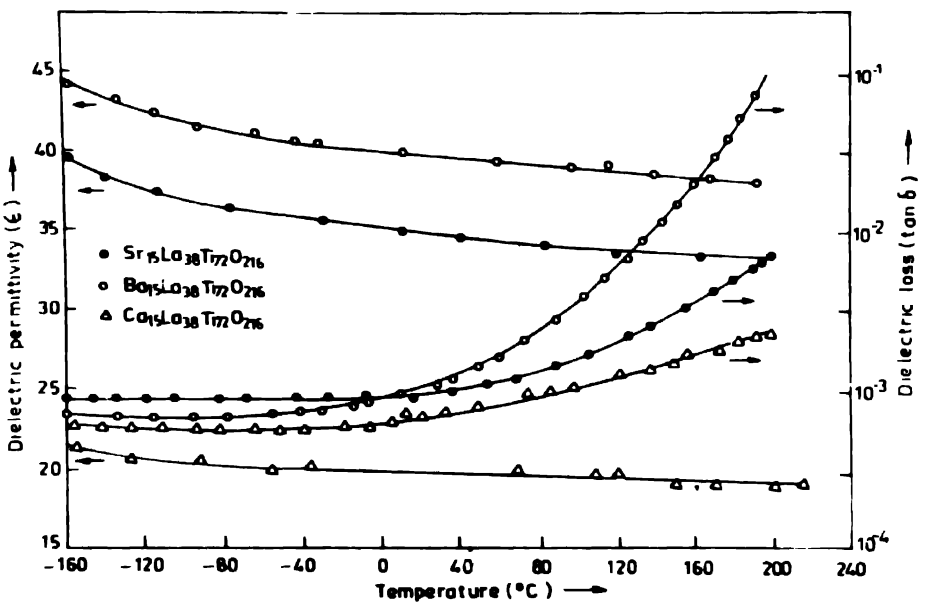

Figure 4. Comparison of temperature dependent ε and tan δ of $A_{1.5}La_{38}Ti_{72}O_{216}$ (A = Sr, Ba, Ca) at 10 KHz.

all the compounds have low dielectric constant and tangent loss at room temperature. In general, ε of all the compounds decrease with increase of temperature whereas dielectric loss (tan δ) increases with increase of temperature. Careful and reapeated measurements of ε and tan δ, even in small temperature interval, did not show any anomaly in any of these title compounds which clearly suggests the non-existence of ferroelectric properties in them.

The temperature dependence of electrical conductivity σ and activation energy E_a of all the samples have been calculated from the dielectric data collected at different temperatures using standard formula

$$\sigma = \varepsilon\, \omega\, \varepsilon_0 \tan \delta \text{ and } \sigma = \sigma_0 \exp(-E_a / k_\beta T) \text{ respectively,}$$

where ε_0 is the dielectric at free space, ω is the angular frequency and k_β is Boltzmann constant. The activation energy (E_a) of all the compounds have been obtained from the slope of the plots ln σ *vs* T^{-1} (Figure 5). The values of the activation energies are tabulated in Table 1. It is observed that (in Figure 5) the conductivity of the samples increases rapidly at high temperature region. So it is clear that at high temperature, there is some oxygen vacancies created and due to this, ionisation takes place inside the samples.

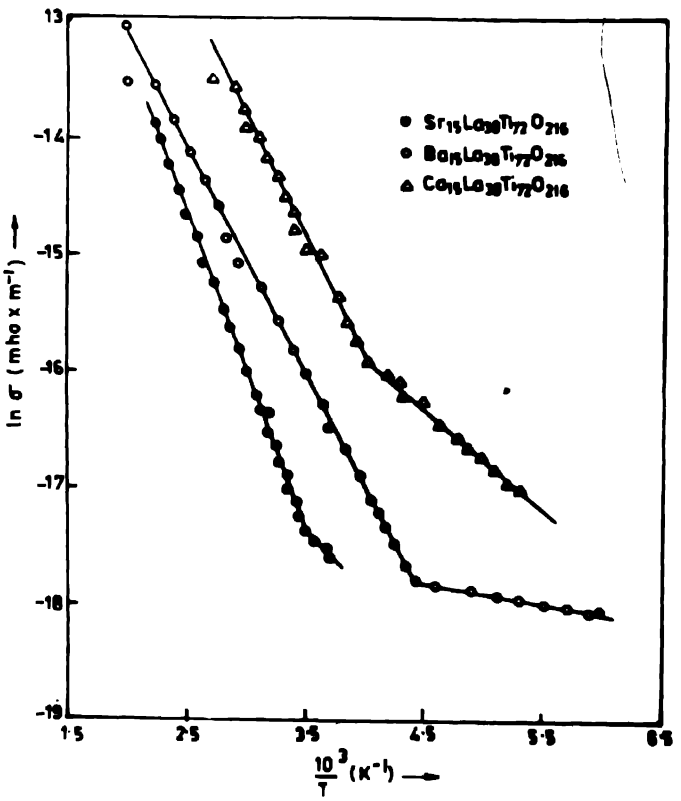

Figure 5. Comparison of electric conductivity (log σ) of $A_{1.5}La_{38}Ti_{72}O_{216}$ *vs* inverse of temperature (T^{-1})

Figure 6 shows the thermal studies (TG, DTA) upto 600°C on powder samples of the titled compounds. The TG and DTA curves did not show any exothermic or endothermic peaks. However, the compounds were found quite stable in this wide temperature range. Finally, it is concluded that the title compounds are in orthorhombic crystal system at room temperature and have no ferroelectric phase transition in the temperature range −160°C to 250°C and are thermally very much stable from room temperature to 600°C.

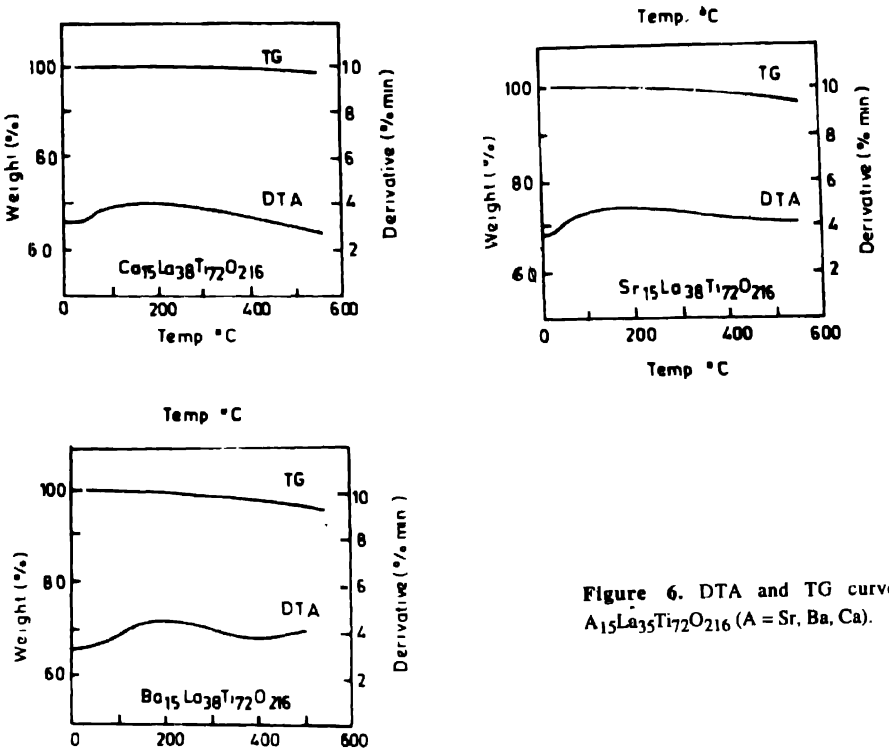

Figure 6. DTA and TG curves of $A_{15}La_{35}Ti_{72}O_{216}$ (A = Sr, Ba, Ca).

Acknowledgment

The authors are thankful to Mr. R P Mukherjee and Mr. Shyamal Mukherjee for their kind experimental help.

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